The effect of pressure on the keto-enol equilibria of acetone and cyclohexanone

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THE EFFECT OF PRESSURE ON THE KETO-ENOL EQUILIBRIA OF ACETONE AND CYCLOHEXANONE

BY JIRO OSUGI, TETUO MIZUKAMI AND TADAFUMI TACHIBANA

The effect of pressure on the keto-enol equilibria of acetone and cyclohexanone in the solvents of carbon disulfide, toluene and *n*-hexane has been studied by the measurement of the infrared spectra at high pressure. Comparing the molal volume of the keto form with that of the enol form, it is expected that the enol from is favorable with increasing pressure. In this study, this expectation has been confirmed. That is, the keto-enol equilibria of acetone and cyclohexanone shift to the enol form with increasing pressure.

However, the absolute value of the enol concentration is yet small. For example, the value of the keto-enol equilibrium constant, K=(enol)/(keto), for acetone in *n*-hexane is 1.6×10^{-2} at a pressure of 8000 kg/cm^2, and that for cyclohexanone in *n*-hexane is 3.6×10^{-2} at the same pressure.

Acetone and cyclohexanone are the monoketones of the aliphatic and the cyclic structure, respectively, and the pressure effect on the keto-enol equilibria is larger for the former than for the latter. This difference may be due to the structural differences between acetone and cyclohexanone.

As for the solvent effect on the keto-enol equilibria, the concentration of the enol form of acetone and cyclohexanone in the solvent of n-hexane are much higher, and in general the enol form increases in *n*-hexane. This tendency is also confirmed in this experiment. The concentration of the enol form of acetone in carbon disulfide and in toluene are much the same, but for cyclohexanone the concentration of the enol form in carbon disulfide is higher than in toluene.

Introduction

Since K. Meyer[1] had determined the concentrations of the enol forms at equilibria for some ketones by the so-called K. Meyer Method which is based upon the fact that the enol form absorbs bromine rapidly, the studies on the keto-enol equilibria were carried out for many substances. The other titration method using iodine monochloride was also reported[2].

The molecular refraction[3], the ultraviolet spectrum[4] and the infrared spectrum[5] were also used as the means of studying the keto-enol equilibria in comparison with the titration method.

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In the studies on the keto-enol equilibria by the infrared spectrum, the $>C=O$ stretching region at about 1700 cm^{-1} and the $>C=C<$ stretching region at about 1600 cm^{-1} were generally used[6]. Especially, the keto-enol equilibrium of ethylacetoacetate was investigated in detail by using those regions.

As for the effect of pressure on the keto-enol equilibria, Kabachnik *et al*[7], and Le Noble[8] studied it for ethylacetoacetate. However, in these studies the concentration of the enol form was determined by the titration method after releasing pressure.

In general, the substances used as samples of the studies on the keto-enol equilibria were ethylacetoacetate or β-diketones. Then, little attention has been paid to the keto-enol equilibria on monoketones.

This paper reports the results obtained from the studies of the pressure effect on the keto-enol equilibria of acetone and cyclohexanone by the measurement of the infrared spectra at high pressure.

Experimentals

Acetone, cyclohexanone and benzaldehyde, and carbon disulfide, toluene and *n*-hexane, commercially offered as guaranteed reagents, treated with the ordinary purification method, were used as the samples, and the solvents, respectively. These solvents were chosen from the view of the following criteria.

1. No absorption band in the experimental range of wave numbers.
2. No solidification at the experimental pressure.
3. No reactivity with the carbonyl group.
4. No corrosive action to the optical vessel.

Then, the polar solvents, such as alcohols, chloroform, methylene chloride, etc., were not used in this study.

The apparatus used is the same as reported in the previous paper[9]. When this optical vessel is used for the measurement of the infrared spectrum, the response of the spectrometer is very slow. Then, after getting balanced positions, the dots of the recorder pen were obtained at the interval of 10~20 cm^{-1}.

The solution of 1 mole/*l* was always used in this experiment, for this concentration was suitable for the measurement of the absorption spectra at high pressure, owing to the path length of the optical vessel.

The measurement was performed at the pressures of 1, 2000, 4000, 6000 and 8000 kg/cm^2 for each solution.

On the other hand, the apparent extinction coefficients of each solution at 3400 cm^{-1} and the relation between the concentration of OH group and the apparent extinction were obtained by using an ordinary optical cell with potassium chloride windows. The experiments were carried out in the room conditioned at 20°C, though the temperature of the optical vessel for high pressure measurement was not regulated by any special method.

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Results and Considerations

Absorption band of the enol OH stretching vibration

Up to the present time, the >C=O stretching region and the >C=C< stretching region were used in the studies on the keto-enol equilibria by the infrared spectrum[6]. However, these regions are not used in this study, since the sapphire window has no transmittance in these regions.

It was reported that the enol OH stretching vibrations of ethylacetoacetate and β-diketone such as acetylacetone were found in 2500~2800cm^{-1}[10]. This fact was explained from the view that the enol OH group in these substances would form the conjugate chelation with the strong intramolecular hydrogen bond, because of the shift of the OH stretching vibration to the lower wave number.

However, Calvert *et al*[11]. reported that the OH absorption band of the enol acetone in the photolysis of 2-pentanone vapor was found at 3629cm^{-1} in vapor phase. Accordingly, since methanol has the absorption band of OH at 3682 cm^{-1} in vapor phase and phenol has an analogous structure to the enol

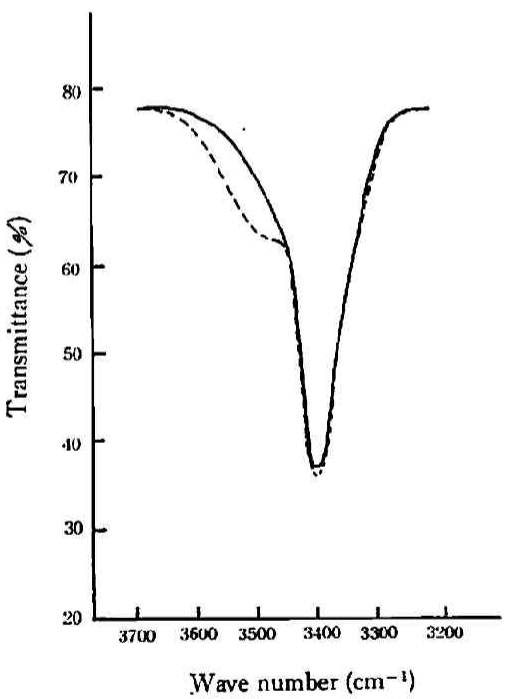

Fig. 1 Spectra of acetone and methanol in acetone. (0.05 mole/*l*)
Full line : acetone
Broken line : methanol in acetone

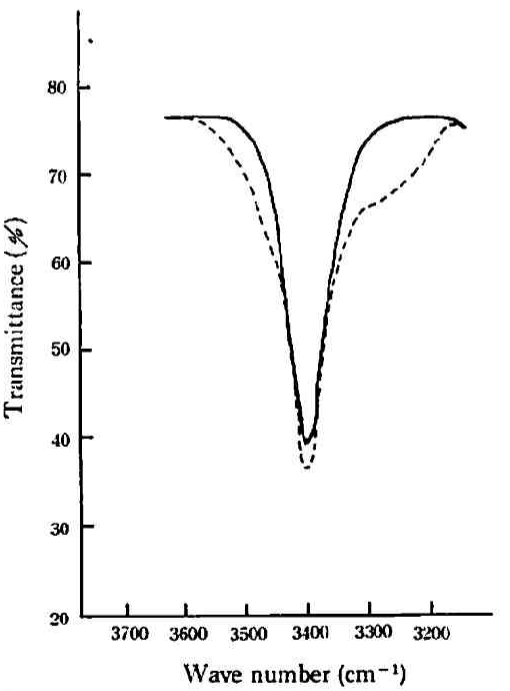

Fig. 2 Spectra of cyclohexanone and phenol in cyclohexanone (0.05 mole/*l*)
Full line : cyclohexanone
Broken line : phenol in cyclohexanone

10) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, *J. Am. Chem. Soc.*, 71, 1068 (1949)
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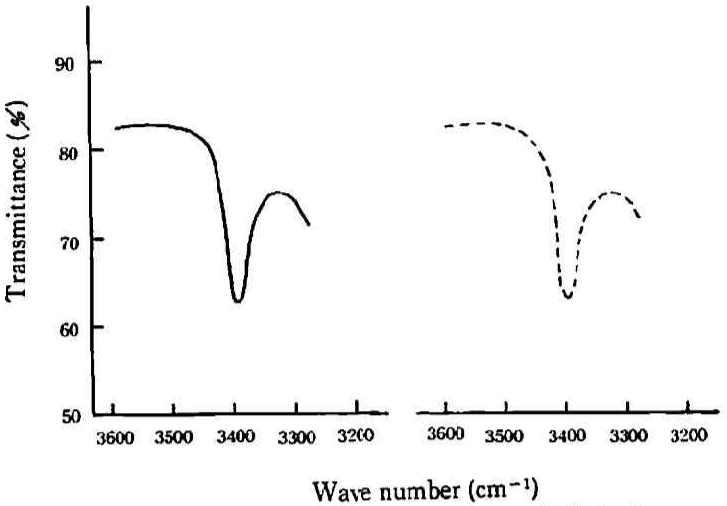


Fig. 3 Spectra of acetone in *n*-hexane at 2000 kg/cm²
Full line : after 2 hours
Broken line : after 20 hours

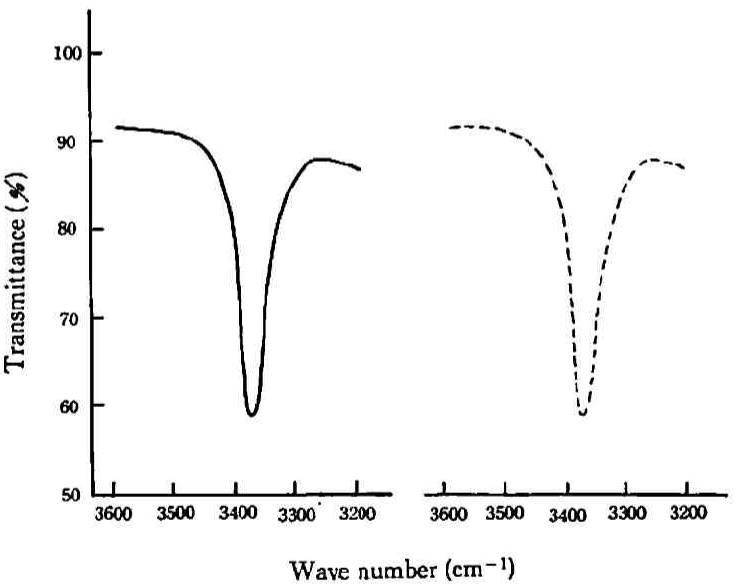


Fig. 4 Spectra of cyclohexanone in carbon disulfide at 8000 kg/cm²
Full line : after 2 hours
Broken line : after 20 hours

form of cyclohexanone, methanol in acetone and phenol in cyclohexanone have the infrared spectra as shown in Figs. 1 and 2, respectively.

The absorption band at 3400 cm^{-1} in these spectra is the overtone band of $>C=O$ stretching vibration. However, as shown in Figs. 1 and 2, it is assumed that the enol OH absorption bands of acetone

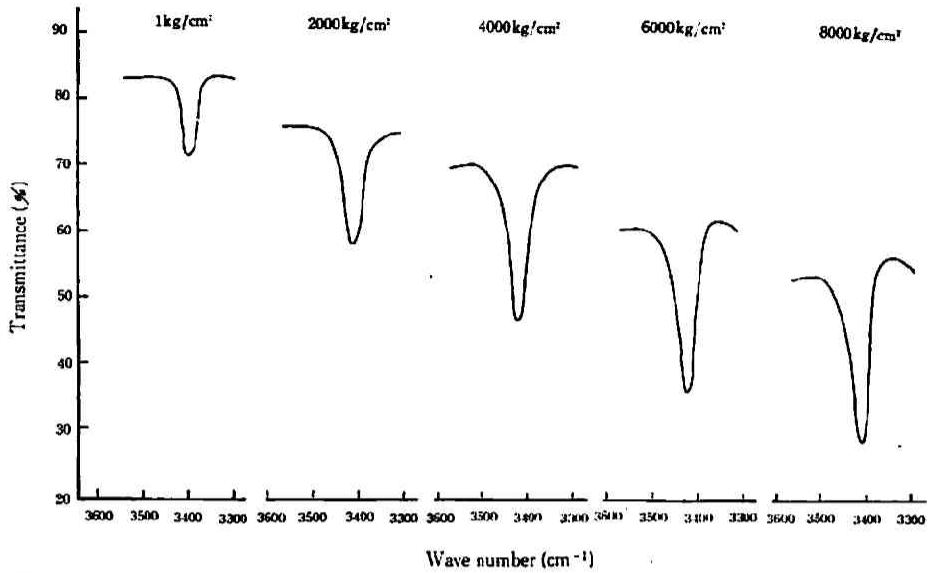


Fig. 5 Change of the apparent transmittance of the spectra of acetone in toluene by pressure (1 mole/*l*)

and cyclohexanone overlap with the overtone band, respectively. Then, the effect of pressure on the absorption band at 3400cm^{-1} was studied.

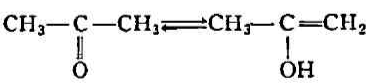
Time required to reach at equilibrium after compression

The time required to reach at equilibrium after compression is examined. As shown in Figs. 3 and 4, there is no difference between the spectrum after 2 hours at the definite pressure and that after 20 hours, and the system is allowed to reach at equilibrium in 2 hours, so that measurements of the spectra were carried out after 2 hours' pressing.

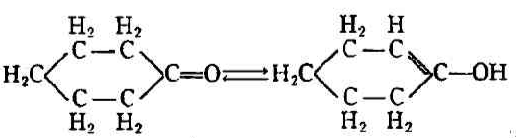
Effect of Pressure on the keto-enol equilibrium

The apparent absorptions at 3400cm^{-1}, of 1 mole/*l* solutions of acetone, cyclohexanone and benzaldehyde in the solvents of carbon disulfide, toluene and *n*-hexane were measured at the pressures of 1, 2000, 4000, 6000 and 8000kg/cm^2. The result obtained for acetone in toluene is shown in Fig. 5 as an example.

Acetone and cyclohexanone may be in the keto-enol equilibrium as shown in equations (1) and (2), respectively.



(1)



(2)

The molal volume of acetone is 73.3cm^3 and that of allyl alcohol, $CH_2{=}CH{-}CH_2OH$, which is the

alcohol type isomer of acetone, is 68.0 cm^3. The latter is smaller than the former. On the other hand, the parachors[12] of the keto forms and the enol forms of acetone and cyclohexanone are calculated. The parachor is represented by equation (3),

$$P=\frac{M\cdot\gamma^{\frac{1}{4}}}{D-d} \qquad (3)$$

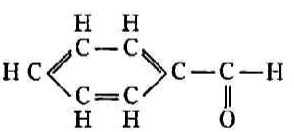
where M is the molecular weight, γ is the surface tension, D is the density of liquid phase and d is that of gas phase. In equation (3), in the keto form and the enol form, M is the same, d being negligible by comparing with D and assuming to be $\gamma_e^{\frac{1}{4}}\fallingdotseq\gamma_k^{\frac{1}{4}}$. Then, equation (4) is deduced. In equation (4) suffixes e and k represent the the enol form and the keto form, respectively.

$$D_e=\frac{D_k\cdot P_k}{P_e} \qquad (4)$$

The density of the enol form is calculated by equation (4). Then, the molal volume of the enol form is estimated. The results are shown in Table 1. That is, the molal volumes of the enol forms of acetone and cyclohexanone are smaller than those of the keto forms, respectively. The molal volume of the enol form of acetone calculated by the parachor is essentially equal to that of allyl alcohol.

Accordingly, it is expected that the keto-enol equilibrium shifts to the enol side with increasing pressure. As shown in Fig. 5, the apparent absorptions increase with pressure. It is considered that the increases of the apparent absorptions of acetone and cyclohexanone are due to the shift of the keto-enol equilibria to the enol side.

However, the tendency that the apparent absorption increases with pressure was also found in the previous paper[9]. In order to study the influence of pressure on the overtone band of $\rangle C{=}O$ stretching vibration, the apparent absorptions at 3400cm^{-1} of benzaldehyde, which has not the enol form the view point of the molecular structure, were measured in the solvents under high pressure.



benzaldehyde

On the other hand, the apparent extinction coefficients of these samples at 3400 cm^{-1} were obtained in each solvent. The results are shown in Table 2.

Table 1 Calculated molal volume at 20°C

	Type	Parachor	Density (g/cm^3)	Molal volume (cm^3/mole)
acetone	keto	161.4	0.792	73.3
	enol	148.9	0.858	67.7
cyclohexanone	keto	250.8	0.947	103.6
	enol	238.3	0.997	98.3
allyl alcohol			0.854	68.0

12) O. R., Quayle *Chem. Rev.*, 53, 439 (1953)

Table 2 Apparent extinction coefficient at 3400 cm^{-1} (ε_a: l/mole.cm)

Solvent	Acetone	Cyclohexanone	Benzaldehyde
carbon disulfide	7.51	7.69	7.81
toluene	6.85	7.64	9.21
n-hexane	7.91	7.63	11.24

Table 3 E_a

	Solvent	Pressure (kg/cm^2)				
		1	2000	4000	6000	8000
acetone	carbon disulfide	7.51	11.5	15.0	19.9	23.4
	toluene	6.85	12.4	19.3	25.6	31.5
	n-hexane	7.91	13.3	19.6	26.7	33.2
cyclohexanone	carbon disulfide	7.69	12.6	18.1	20.6	25.9
	toluene	7.64	13.9	20.4	25.4	32.0
	n-hexane	7.63	12.6	18.9	24.5	30.8
benzaldehyde	carbon disulfide	7.81	10.4	12.1	14.7	18.1
	toluene	9.21	14.2	19.1	23.0	29.0
	n-hexane	11.24	14.3	20.7	23.6	28.0

Supposing that Beer's law (5) holds, the change of the apparent extinction with pressure is calculated by equation (6) from the experimental results. In equation (6), ε_a is the apparent extinction coefficient, T_P is the transmittance at pressure of P, and T_1 is that of 1 kg/cm^2. E_a is shown in Table 3.

$$\varepsilon cd = \ln \frac{I_0}{I} \tag{5}$$

$$E_a = \varepsilon_a \frac{\log T_P}{\log T_1} \tag{6}$$

The relative volumes of the samples and the solvents are shown in Table 4. The values for acetone, carbon disulfide and *n*-hexane are the data of P. W. Bridgman[13], but those for toluene, cyclohexanone

Table 4 Relative volume at 20°C (V_P/V_1)

	pressure (kg/cm^2)				
	1	2000	4000	6000	8000
acetone	1.000	0.887	0.786	0.786	0.768
cyclohexanone	1.000	0.901	0.846	(0.818)	(0.806)
benzaldehyde	1.000	0.915	0.867	(0.835)	(0.820)
carbon disulfide	1.000	0.896	0.843	0.811	0.784
toluene	1.000	0.896	0.844	0.800	0.772
n-hexane	1.000	0.864	0.812	0.778	0.753

13) P. W. Bridgman, "The Physics of High Pressure," p. 128 (1958)

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and benzaldehyde were measured in our laboratory. Pure cyclohexanone and benzaldehyde solidify at pressures of 4400 and 4700kg/cm², respectively. However, it is found that they do not solidify in solutions at a pressure of 8000 kg/cm². but they may be in super compressing. Then, the relative volumes of these samples at pressures of 6000 and 8000 kg/cm² were obtained by the extrapolations of volume-pressure curves below the freezing points.

E'_a is the apparent extinction obtained by equation (7).

$$E'_a = E_a \times \frac{V_P}{V_1} \qquad (7)$$

E'_a is the value which is corrected for the change of the concentration due to compression. Plotting E'_a against pressure, the linear relations were obtained as shown in Figs. 6~8. In Figs. 6~8, the apparent extinction of benzaldehyde also increases with pressure. But, as benzaldehyde does not change to the enol form from the view point of its molecular structure as described above, it is concluded that the increase of the apparent extinction of benzaldehyde is brought by pressure itself, and not by the enol form.

It is assumed that the coefficient of the change of the apparent extinction of each sample by pressure itself would be equal in the same solvent. Accordingly, the increase of the apparent extinction of the OH group due to the shift of the keto-enol equilibrium to the enol side with increasing pressure is represented by the difference between the increment of the apparent extinction of acetone or cyclohexanone by pressure and the increment which multiplied the apparent extintion of acetone or cyclohexanone at ordinary pressure by the pressure coefficient of the benzaldehyde in the same solvent.

This relation is represented by equation (8), where E_{a0} is the apparent extinction of the OH group, E'_{sap} and E'_{as1} are the E'_a for acetone,

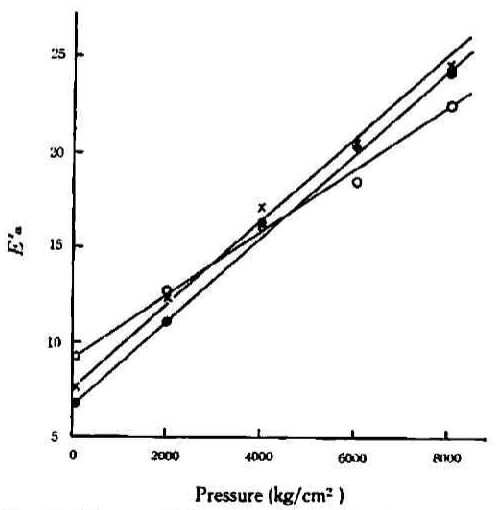

Fig. 7 Change of the apparent extinction at 3400 cm⁻¹ by pressure
● : acetone in toluene
× : cyclohexanone in toluene
○ : benzaldehyde in toluene

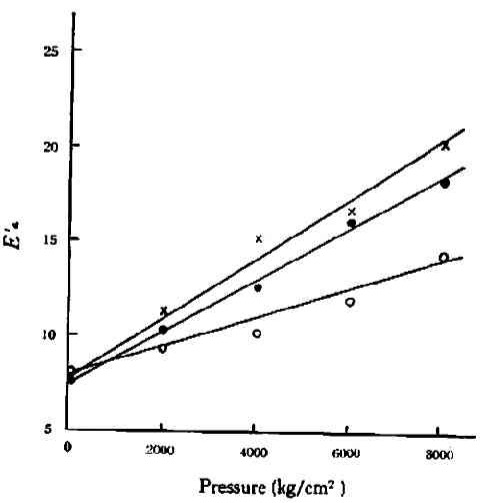

Fig. 6 Change of the apparent extinction at 3400 cm⁻¹ by pressure
● : acetone in carbon disulfide
× : cyclohexanone in carbon disulfide
○ : benzaldehyde in carbon disulfide

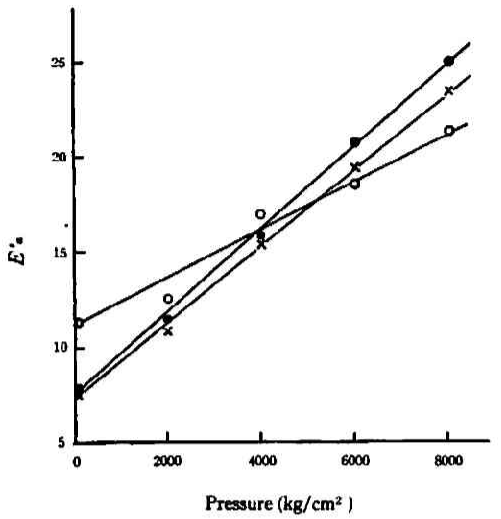

Fig. 8 Change of the apparent extinction at 3400 cm^{-1} by pressure
● : acetone in *n*-hexane
× : cyclohexanone in *n*-hexane
○ : benzaldehyde in *n*-hexane

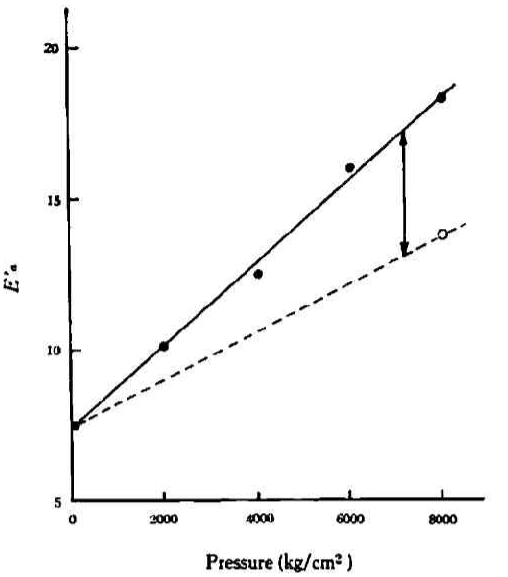

Fig. 9 Correction for the change of the apparent extinction by pressure
Full line : acetone in carbon disulfide
Broken line : correction line

$$E_{a0}=E'_{ap}-\frac{E'_{a1}\cdot E'_{ab}}{E'_{ab1}} \qquad (8)$$

or cyclohexanone at pressures of P and 1 kg/cm², respectively, and E'_{abp} and E'_{ab1} are those of benzaldehyde. For example, in the case of acetone-carbon disulfide system (Fig. 9), the value of the apparent extinction shown by arrow line is the apparent extinction of the enol OH group which is increased by pressure.

However, E_{a0} involved the change of the apparent extinction by pressure itself as mentioned above. Accordingly, the correction is carried out by equation (9). The relation is shown in Fig. 10.

$$E'_{a0}=\frac{E_{a0}\cdot E'_{ab1}}{E'_{abp}} \qquad (9)$$

The value of E'_{c0} is the apparent extinction of the OH group which is increased by the shift of the keto-enol equilibrium to the enol side in equations (1) and (2) by pressure.

On the other hand, using the low concentration solutions of methanol in acetone and phenol in cyclohexanone, the apparent extinction of the OH group in ketones was measured. The result is shown in Fig. 11. That is, the apparent extinction of methanol in acetone is in good agreement with that of phenol in cyclohexanone. Accordingly, it is not unreasonable that this relation between the apparent extinctions and the concentrations of these substances is used for the estimation of the concentration of the enol OH group. Then, the concentration of the enol form was determined by this relation. The result is shown in Table 5 as the keto-enol equilibrium constant.

The ratio of the increase of the keto-enol equilibrium constant with pressure is larger for acetone than for cyclohexanone. These increases with pressure are shown in Figs. 12 and 13.

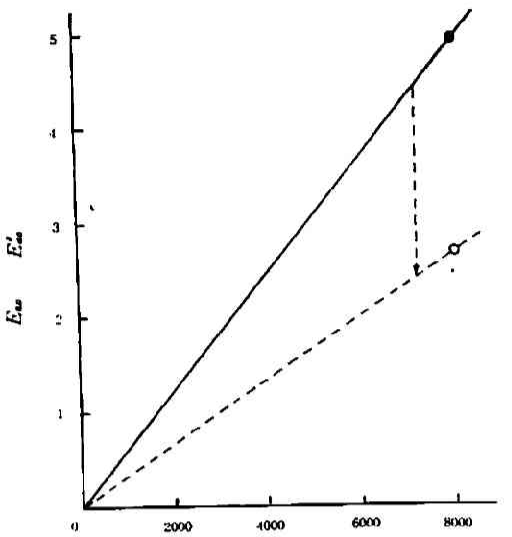

Fig. 10 Correction for the change of the apparent extinction by pressure
Full line : E_{a0}
Brocken line : E'_{a0}

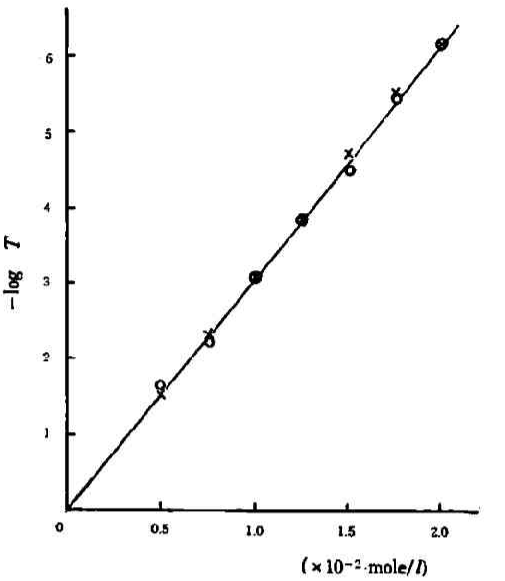

Fig. 11 Relation between the concentration and the apparent extinction of OH group
× : methanol in acetone
○ : phenol in cyclohexanone

Table 5 Equilibrium constant at 20°C

	Solvent	Pressure (kg/cm²)				
		1	2000	4000	6000	8000
$K_a \times 10^3$	carbon disulfide	0.32	2.36	4.47	6.59	8.57
	toluene	0.40	2.46	4.57	6.70	8.75
	n-hexane	0.62	4.37	8.42	12.71	16.50
$K_c \times 10^2$	carbon disulfide	2.05	2.36	2.64	2.95	3.24
	toluene	2.04	2.31	2.55	2.80	3.05
	n-hexane	2.09	2.44	2.83	3.22	3.60

K_a=(enol)/(keto) (acetone)
K_c=(enol)/(keto) (cyclohexanone)

ΔV obtained by equation (10) is shown in Table 6. On the value

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V}{RT} \tag{10}$$

of ΔV, there is a large difference between acetone and cyclohexanone. It is concluded that this difference is owing to the aliphatic structure of acetone and the cyclic structure of cyclohexanone. In the molal volumes of the keto form and the enol form of these substances calculated by the parachors, the differences between the keto form and the enol form are much the same for these substances. However, for the enol

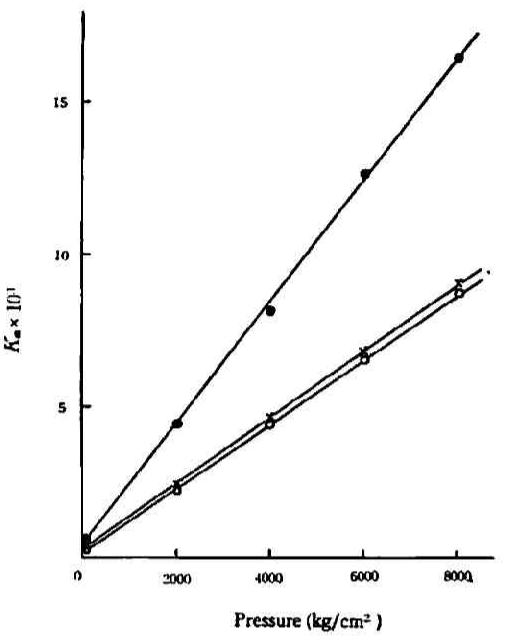

Fig. 12 Effect of pressure on the keto-enol equilibrium constant of acetone in solvent
● : *n*-hexane
○ : carbon disulfide
× : toluene

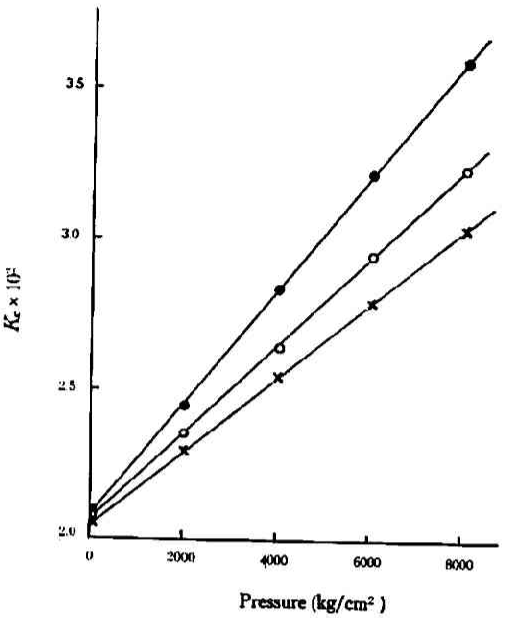

Fig. 13 Effect of pressure on the keto-enol equilibrium constant of cyclohexanone in solvent
● : *n*-hexane
○ : carbon disulfide
× : toluene

Table 6 ΔV (cm³/mole)

	Solvent	Pressure (kg/cm²)				
		1	2000	4000	6000	8000
acetone	carbon disulfide	−21.4	−10.8	−5.3	−3.4	−2.4
	toluene	−21.6	−11.2	−5.3	−3.1	−2.4
	n-hexane	−23.2	−11.7	−5.8	−3.8	−2.6
cyclohexanone	carbon disulfide	−2.1	−1.5	−1.3	−1.2	−1.0
	toluene	−1.8	−1.3	−1.1	−1.0	−0.9
	n-hexane	−2.5	−1.7	−1.5	−1.3	−1.2

form of cyclohexanone, the >C=C< double bond should be produced in the six membered ring. Owing to this double bond the striction is made in the six membered ring. For this reason it is supposed that the shift to the enol form is retarded. On acetone, as there is no steric hindrance, the ratio of the enolization is higher comparing to cyclohexanone. From the view that acetone is in associated state. the value of ΔV for acetone is understandable.

As for the solvent effect, the enolization of acetone or cyclohexanone is highest in *n*-hexane. It was previously reported that the concentration of the enol form increased in *n*-hexane. This tendency was

also confirmed in this study. The enolization of acetone in carbon disulfide and in toluene are much the same, but that of cyclohexanone in carbon disulfide is larger than in toluene. This may be ascribed to the effect of the steric factor on the keto-enol equilibrium.

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